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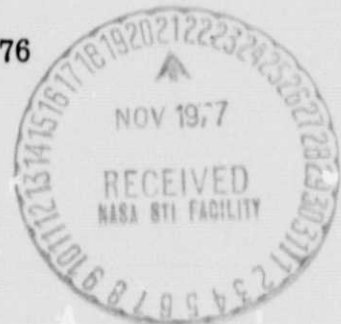
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**CONSOLIDATION OF SILICON NITRIDE
WITHOUT ADDITIVES**

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INTRODUCTION

Ceramics are being considered for gas turbine engine applications because present day metallic alloys are rapidly approaching the limits of their temperature capabilities. Two of the most promising ceramics currently being investigated are Si_3N_4 and SiC . These materials possess many attractive features chief of which are low density, low thermal expansion, and good high temperature strength. Moreover they are made from elements relatively abundant on the earth's surface. However, there are several unattractive features possessed by these materials such as brittleness, poor impact resistance, and difficulty in consolidation.¹ Our efforts in this study were directed toward producing dense Si_3N_4 .

Because of its covalent bonding nature, conventional sintering methods cannot produce dense Si_3N_4 bodies.² In general the two most common methods of consolidating Si_3N_4 currently being used are: (1) hot pressing (2) reaction sintering. Fully dense bodies can be obtained from the hot pressing approach only when a sintering aid, such as MgO , is used. Hot pressing requires the use of high temperatures, 1650° to 1800° C, and uniaxially applied pressures, 4000 to 6000 psi ($27.5\text{--}41 \text{ MN/m}^2$) in special dies such as graphite. Reaction sintering cannot produce fully dense bodies and is done at a lower temperature, 1250° to 1400° C, without the use of sintering aids. Bodies prepared by hot pressing are usually limited in shape to simple geometric patterns, and therefore require costly subsequent machining, whereas more complex shapes, blades, vanes, etc. may be produced directly by reaction sintering, with a density in the range of 70% to 80% of theoretical density (T.D.). The density attained in hot pressed Si_3N_4 bodies is believed to be the result of the formation of a glassy phase at the grain boundaries.³ This glassy phase has been found to be the cause of the decline in high temperature strength of bodies so prepared.⁴ To retain strength at high temperatures it would appear to be desirable to produce fully dense bodies of Si_3N_4 without the use of additives.

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This investigation was undertaken to determine the feasibility of producing a sound, dense Si_3N_4 body without additives, using conventional gas hot isostatic pressing techniques and an uncommon hydraulic hot isostatic pressing technique. These two HIPPING techniques produce much higher pressure 275-413 MN/m^2 (40,000 - 60,000 psi) than hot-pressing techniques. Evaluation was based on density measurement, microscopic examination, both optical and electron, and X-ray diffraction analysis.

MATERIALS, APPARATUS, AND PROCEDURES

Materials

The Si_3N_4 used in this investigation was purchased from a commercial vendor (AME). Characterization of the powder showed that the material contained two phases, 80% α and 20% β , and had an average particle size of 1.56 μm . A spectrographic analysis of the material is shown in table I.

Hot Isostatic Pressing Techniques

Two approaches to hot isostatic pressing were used in this study. The principles of each technique are shown in figure 1 and are described below.

Gas hot isostatic pressing-gas hippping. - Conventional gas pressure bonding techniques⁵ were used to produce both round specimens 1.25 cm diameter x 5.1 cm (1/2 in. diameter x 2 in.) and rectangular specimens 1 cm x 5.7 cm x 3 cm (0.4 in. x 2 1/4 in. x 1.2). Specimens were first cold pressed into shape and then vacuum incapsulated in molybdenum containers. The HIP facility used in this study uses helium gas and can reach a maximum of 40,000 psi (275 MN/m^2) and 1760° C.

Hydraulic hot isostatic pressing-hydraulic HIPPING. - A hydraulic isostatic press was modified so that densification of a compact could be accomplished at some elevated temperature with a maximum pressure of 413 MN/m^2 (60,000 psi) which is 50 percent higher than the gas hippping pressure used in this study. This work was based on a concept reported by Levey.⁶ A conventional hydraulic isostatic press was modified by the addition of a power feed through and 2 thermocouple feed throughs. This is shown schematically in figure 2. Figure 3 shows details of the bag assembly. It may be seen that a container for a heater and the specimen to be compacted is located within the vessel cavity. This container or bag is loaded with a glass sand which surrounds the heater and specimen and serves as twofold purpose; transmission of the pressure and insulation against heat loss. The specimen itself is incapsulated in either quartz or molybdenum (depending on maximum temperature level of a particular run) to preclude contamination from the sand. This capsule is then surrounded

by the heater coil, in this case Mo wire, and attached to the bag electrical power feedthrough. When this assembly has been properly located, the bag is filled with sand and sealed under vacuum, 0.01 to 0.15 N/m² (10 to 20 torr). The cover, to which the bag is attached, is lowered, immersing the bag in a water solution which fills the vessel; the closure is made, and heating commences. Pressure is applied, when the desired temperature is attained, depending on the heating and pressurization schedule used. Dwell times at temperature and pressure up to 120 minutes were used.

Microscopy

Optical. - Specimens were prepared and examined using conventional techniques on a light microscope.

Transmission electron microscopy (TEM). - Specimens were prepared for TEM by ion bombardment to produce a thin film and were examined on a 100 KV electron microscope.

Density Measurement

A water displacement technique was used to determine the density of the consolidated specimens. Porous specimens were coated with a thin layer of wax before water immersion. The weight and volume of wax were subsequently subtracted from the specimen in calculating the density.

Phase Determination

The phases present in the prepared specimens were determined by standard X-ray diffraction procedures. X-ray peak heights were used to estimate the relative amounts of the phases present.

RESULTS AND DISCUSSION

It was anticipated that high density Si₃N₄ bodies were more likely to be produced with a combination of the maximum temperature and pressure attainable with the two HIPING units available to the investigators. Thus most of the experiments were made using the extreme capacities of the two units. Many such runs were unsuccessful or incomplete due to leaking seals, leaking of sample containers, furnaces burning out, and failure in the hydraulic system. Consequently only the results of a limited number of runs are meaningful. A systematic study of the effects of temperature, pressure and time was not possible at this time. However enough information has been obtained to be of interest to other investigators.

HIPPING Conditions and Density

Table II lists the HIPPING pressure, temperature and time at temperature and pressure, along with the HIPPED specimen density and percent β phase. The same information for the cold isostatically pressed green compact is included in the table for reference. It is apparent from the table that a combination of higher temperature and higher pressure was required to produce a density approaching or higher than 90% T.D. (specimens No. 3, 4, and 7). This represents an increase of 40% T.D. or more from the green compact. As will be discussed later no densification is obtainable at conventional hot pressing pressures at a temperature level (1700° to 1800° C) comparable to the highest HIPPING temperature (1760° C) used in this investigation. Conventionally the hot pressing pressure level is an order of magnitude lower than that of the HIPPING run. This correlation of higher applied isostatic pressure with higher resulting density suggests that the observed densification at elevated temperatures produced by HIPPING was related to increased mechanical work done to the specimen. The TEM results which will be discussed in more detail later show evidence of dislocation tangles suggesting that plastic deformation had indeed occurred in the densified specimen. This was not observed in Si_3N_4 bodies prepared by hot-pressing with additives or reaction-sintering.

If plastic yielding were the major mechanism for densification, then densification should not be dependent on the length of time the specimen was held at temperature and pressure. However, the second densest body (specimen No. 7) produced in this study was made at a relatively low temperature (1260° C) and pressure (45 ksi), (310 MN/m^2) but was held for the longest period of time (2 hours) among all the runs. The effect of time at temperature and pressure is more clearly demonstrated by the increase in density from specimen No. 5 to No. 7, both of which were HIPPED at approximately the same pressure and in the same temperature range, but for an increasing length of time. This observation leads us to propose that if the HIPPING temperature and pressure used were high enough to produce rapid plastic deformation in the specimen, densifying it to a certain intermediate density, then a slower time-dependent phenomenon would continue to densify the specimen. The fine equiaxed grains, some containing twins, which were found in TEM examination suggest that recrystallization occurred under the applied pressure which could explain the observed time-dependent densification. Further discussion of this concept will be presented in the next two sections.

α To β Phase Transformation

It is of interest in table II that almost all the starting α -phase had transformed to β -phase in the higher density specimens. Furthermore there is a definite relationship between the relative amount of β -phase present and the specimen density as shown in figure 4. It is therefore

reasonable to postulate that the observed α to β phase transformation accompanying the densification process, was caused by the same extrinsic parameters as the ones which caused the densification process, a combination of high enough temperature and pressure plus long enough time.

At this point, it should be remembered that the cold isostatically pressed Si_3N_4 green compact was encapsulated in a sealed container to which subsequent isostatic pressure was applied at high temperature (HIPING). As the container was under high isostatic pressure and began to deform (contract) at elevated temperature, the individual Si_3N_4 particles (angular in shape) within the container were subjected to high local stresses where in contact with their respective adjacent particles. The magnitude of the local stress developed between the neighboring particles undoubtedly exceeded the level of the isostatic stress applied to the specimen container. Plastic deformation of the individual particles resulting from such high stresses produced the initial densification by bringing the centers of particles closer. The writers postulate that, analogous to the recrystallization phenomenon in metals, strain-free grains would be formed from the plastically deformed grains in order to release the stored strain energy. These recrystallized grains were formed at elevated temperatures and therefore should crystallize to the $\beta\text{-Si}_3\text{N}_4$ structure, the high temperature modification of Si_3N_4 . This proposed recrystallization concept could explain not only why the densification was time-dependent but also why more α to $\beta\text{-Si}_3\text{N}_4$ transformation occurred in higher density specimens. More evidence supporting the recrystallization concept will be found in the next section.

TEM Microscopy

Figure 5 shows the TEM microstructures of specimen No. 2 (60% T.D.) and specimen No. 7 (94% T.D.). In specimen No. 2 (fig. 5(a)) voids are abundant and no evidence of dislocations can be found in the micrograph. The grain morphology retains the flake and fiber-like features of the starting powders. Figure 5(b) is the microstructure of specimen No. 7. The presence of dislocations are apparent in the larger grains, whereas twins are often found in the smaller dislocation-free grains (recrystallized $\beta\text{-Si}_3\text{N}_4$). The presence of twins is strong evidence supporting the recrystallization concept. Figure 5(c) shows a detailed dislocation net work in one of the largest grains in specimen No. 7.

Effect of Impurities

It should be noted that the impurity level of the starting material was not the lowest available. In order to determine whether these impurities alone could promote full densification, several attempts were

made to conventionally hot press 27.5 MN/m^2 (4000 psi) and 1700° to 1800° C the starting powder without any further additives. These attempts resulted in the formation of an easily breakable cake without bonding.

This suggests that the impurities were either not effective sintering aids or not concentrated enough to cause full densification during conventional hot pressing. However, we could not independently determine their role in high pressure HIPING. Therefore the possibility remains that impurities may be contributing to densification during HIPING.

CONCLUDING REMARKS

The goal of this investigation was to consolidate Si_3N_4 without additives and it was indeed attained. Although the data were limited in scope, some areas of interest for future investigation became evident. For example, the evidence of deformation and crystallization should be further explored so that full density and complete recrystallization are attained. Much of the success in this area will be dependent on improved reliability of the high pressure equipment and the canning procedures.

SUMMARY

1. Si_3N_4 can be densified to high density, greater than 95% of theoretical, without additions.
2. The higher density Si_3N_4 specimens appear to be associated with a greater amount of $\alpha \rightarrow \beta$ transformation.
3. Under high pressure, the $\alpha \rightarrow \beta$ transformation can occur at a temperature as low as 1150° C .
4. Grain deformation and subsequent recrystallization and grain refinement result from hot isostatic pressing of Si_3N_4 .

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5. S. J. Paprocki, E. S. Hodge, and P. J. Gripshover, "Gas-Pressure Bonding," DMIC-159, Defense Metals Information Center, Sept. 1961.
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TABLE I. - SPECTROGRAPHIC ANALYSIS FOR IMPURITIES IN α - Si_3N_4 POWDER^a

Element	Content
Al	2000 ppm
B	<100
Ca	500
Cr	<50
Cu	100
Fe	4000
Mg	30
Na	<4000
Ti	250
W	<50
O ₂	^b 2.3%

^a80% α - Si_3N_4 ; 20% β - Si_3N_4 ; average particle size; 1.56 μm

^bVacuum fusion analysis

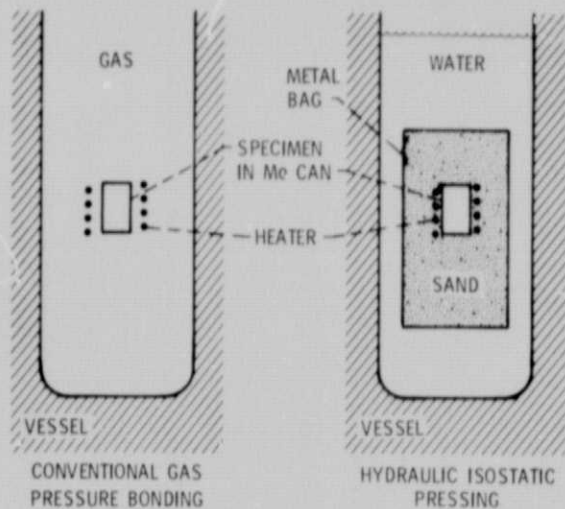
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TABLE II. - RESULTS OF HOT ISOSTATIC PRESSING OF Si_3N_4

Specimen number	Type of HIPING	Temperature, °C	Pressure, ksi (MN/m^2)	Time, hr	Density, % T.D.	Beta phase, percent
^a 1	Hydraulic	Room temperature	70 (482)	0.25	51	20
2	Gas	1550-1620	19.5-22 (134-151)	1	80	50
3	Gas	1760	40 (275)	1	89	90
4	Gas	1760	40 (275)	1	95	100
5	Hydraulic	1150-1290	48.5 (334)	0.75	63	--
6	Hydraulic	>960	59.5 (410)	1.5	79	35
7	Hydraulic	1260	45 (310)	2.0	94	91

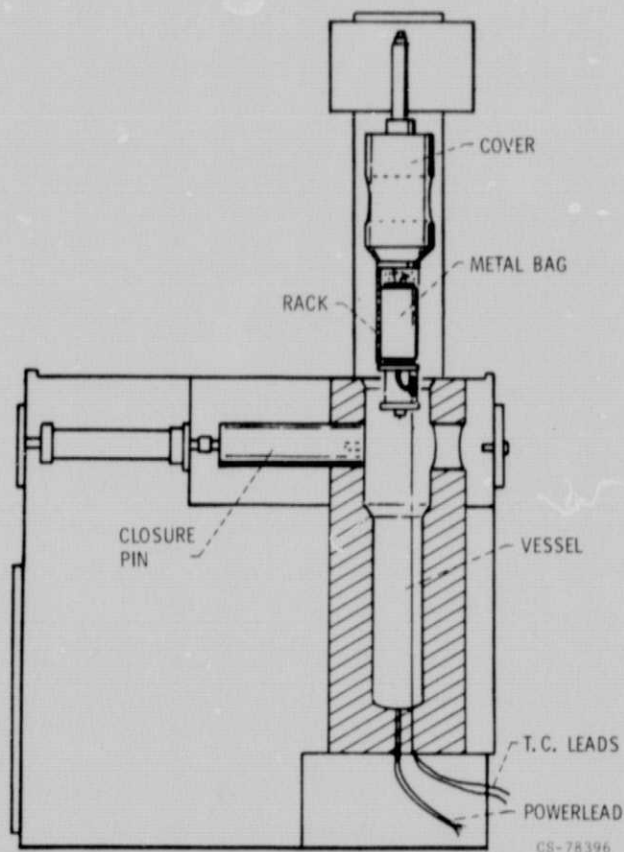
^aAs cold isostatically pressed green compact.

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Figure 1. - Hot isostatic pressing techniques.



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Figure 2. - Modified hydraulic isostatic press.

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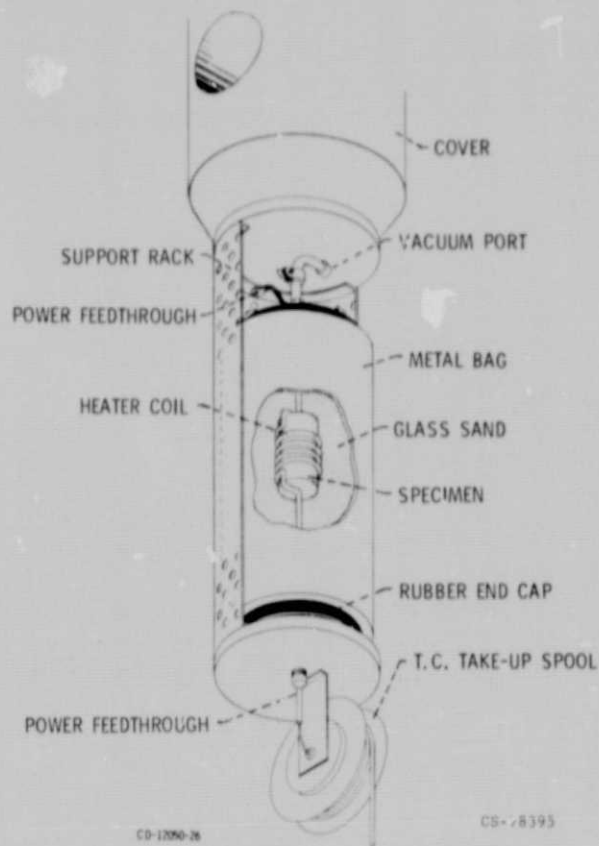


Figure 3. - Bag assembly for hydraulic isostatic pressing.

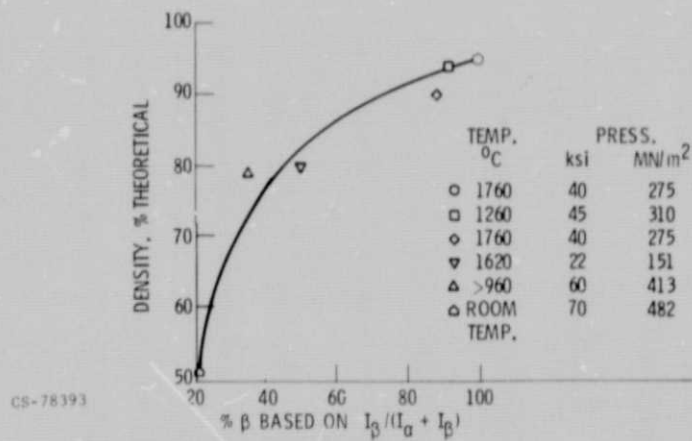
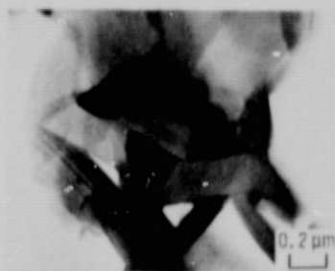


Figure 4. - Relationship of density to $\alpha \rightarrow \beta$ transformation.

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(a) HIPPED AT 1620°C + 22 KSI; 80% T-D
(SPECIMEN NO. 2).



(b) HIPPED AT 1260°C + 45 KSI; 94% T-D
(SPECIMEN NO. 7).



(c) HIPPED AT 1260°C + 45 KSI; 94% T-D
(SPECIMEN NO. 7).

Figure 5. - Electron micrographs showing morphological changes with increasing density.

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